

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 343 523
A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89109014.4

(51) Int. Cl. 4: C09K 3/10 , C08G 18/10

(22) Date of filing: 19.05.89

(30) Priority: 23.05.88 US 197493

(43) Date of publication of application:
29.11.89 Bulletin 89/48

(84) Designated Contracting States:
DE FR GB

(71) Applicant: TREMCO INCORPORATED
10 701, Shaker Boulevard
Cleveland, Ohio 44104(US)

(72) Inventor: Bandlish, Baldev K.
4633 Bradford
S. Euclid Ohio 44121(US)

(74) Representative: von Kreisler, Alek,
Dipl.-Chem. et al
Patentanwälte Von Kreisler-Selting-Werner
Deichmannhaus am Hauptbahnhof
D-5000 Köln 1(DE)

(54) Sealant compositions or coating mixtures containing functional silane or siloxane adhesion promoters nonreactive with blocked isocyanates.

(57) A sealant or coating composition admixture contains a blocked isocyanate-terminated prepolymer in which generally all of the NCO groups are blocked, a curing agent such as a polyamine or a polyimine, and a functional silane or siloxane nonreactive with blocked isocyanates. The sealants or coating compositions when cured have improved properties such as adhesion.

EP 0 343 523 A2

SEALANT COMPOSITIONS OR COATING MIXTURES CONTAINING FUNCTIONAL SILANE OR SILOXANE ADHESION PROMOTERS NONREACTIVE WITH BLOCKED ISOCYANATES

FIELD OF THE INVENTION

The present invention relates to a sealant or coating composition containing a blocked isocyanate-terminated prepolymer, a polyamine or polyimine curing agent, and small amounts of functional silane or siloxane adhesion promoters which are nonreactive with blocked isocyanates. The sealant or coating compositions of the present invention are essentially free of any organosilanes which are reactive with the blocked isocyanate-terminated prepolymer.

BACKGROUND

Sealant and coating compositions desirably have a combination of properties which render them particularly suitable for their intended applications. Such compositions should be able to be packaged in sealed containers or cartridges and stored for relatively long periods of time without objectionable "setting up" or hardening, that is curing of the components in the package. The one component sealant composition should form a relatively tack-free surface upon application and upon exposure to atmospheric moisture should cure without the formation of bubbles within a suitable time. The two component system can be formulated into package stable systems with adjustable cure rate and cured sealant properties. When cured, they should adhere tenaciously to a wide variety of surfaces such as glass, aluminum, concrete, marble, and steel. They should also have sufficient elasticity and flexibility to withstand contraction and expansion of panels, and the like, generally associated with temperature variations as a result of climatic changes and/or wind forces.

U. S. Patent No. 4,067,844 to Barron et al relates to polyurethane polymers in which a proportion of the isocyanate-terminated prepolymers are reacted with certain aminosilanes, or with the reaction product of a mercaptosilane with monoepoxide, or with the reaction product of an epoxysilane with a secondary amine.

U. S. Patent No. 4,507,443 to Barron et al relates to a sealant or a coating composition containing a blocked isocyanate-terminated prepolymer in which generally all of the NCO groups are blocked, a multifunctional imine curing agent, and an organosilane which is reactive with the blocked isocyanate.

U. S. Patent No. 2,942,019 to Pike et al relates to organosilicon methyldieneamino compounds and a process for producing the same.

U. S. Patent No. 3,248,371 to Damusis relates to low temperature deblocking agents which are alkylene oxide adducts of tertiary amines and hydroxy-terminated tertiary nitrogen-containing polyether-based urethane intermediates.

U. S. Patent No. 3,267,078 to Damusis relates to polyether urethane coating compositions which are cured with diimine compounds.

U. S. Patent No. 3,627,722 to Selter relates to urethane sealant compositions in which part of the NCO groups are end-blocked with $-\text{Si}(\text{OR})_3$ groups where R is a lower alkyl.

U. S. Patent No. 4,222,925 to Bryant et al relates to a sealant composition made from a polyurethane containing a small amount of N-beta aminoethyl, gamma-aminopropyltrimethoxysilane and a reinforcing filler such as carbon black.

U. S. Patent No. 4,345,053 to Rizk et al relates to a moisture curable silicon terminated organic polymer made by reacting a polyurethane prepolymer having terminal active hydrogen atoms with an isocyanato organosilane having at least one hydrolyzable alkoxy group bonded to the silicon polymer.

U. S. Patent No. 4,374,237 to Berget et al relates to curable isocyanate prepolymers wherein a portion or all of the available isocyanate terminal groups have been reacted with a secondary amine-containing silane monomer having two trialkoxysilane groups.

U. S. Patent No. 4,625,012 to Rizk et al relates to methods of making moisture curable polyurethane polymers having terminal isocyanate groups and pendant alkoxy silane groups by reacting an isocyanatosilane adduct, having terminal isocyanate groups and at least one hydrolyzable alkoxy group bonded to a silicon, with a polyisocyanate and a polyol.

U. S. Patent No. 4,687,533 to Rizk et al relates to a method for bonding a material to a non-porous substrate such as glass utilizing a moisture curable sealant composition containing a filler and a polyure-

thane polymer having terminal isocyanate groups and pendant silane groups having at least one alkoxy group bonded to silicon.

German Patent 3,414,877 to Emmerling et al relates to moisture hardening polyurethane preparations containing adhesive agents such as aldimine or ketimine group containing alkylalkoxysilanes.

5

SUMMARY OF THE INVENTION

10 According to the concepts of the present invention, improved physical properties such as improved adhesion and improved joint movement capabilities, are achieved when specific types of silanes or siloxanes which are non-reactive with blocked isocyanate groups are utilized. That is, blocked urethane sealants and coatings of the present invention can contain blends of specific types of adhesion promoters which are non-reactive with the blocked isocyanate-terminated groups of the prepolymer. Accordingly, the
15 present invention specifically excludes organosilanes which are reactive with blocked isocyanate-terminated prepolymers. Specific types of functional silanes or siloxanes which are not reactive with blocked isocyanates include epoxysilanes or epoxysiloxanes, isocyanatosilanes or isocyanatosiloxanes and ketiminosilanes or ketiminosiloxanes. The amount of such functional silane or siloxane compounds is generally small, as for example from about 0.1 part to about 10 parts by weight, desirably from about 0.2 to
20 about 1.0 part by weight for every 100 parts by weight of the blocked prepolymer. When sealant compositions are made, a preferred range is from about 0.3 to about 0.7 parts by weight for every 100 parts by weight of the blocked prepolymer.

Sealants or coating compositions of the present invention can be moisture curable and form compositions that adhere tenaciously to a wide variety of surfaces and form tack-free surfaces after being exposed
25 to the atmosphere for only a short period of time. When a two-part system is utilized, mixture of the two separate components forms a cured sealant within a matter of hours after application.

DETAILED DESCRIPTION OF THE INVENTION

30

The present invention relates to a urethane sealant composition or coating admixture comprising a blend of a blocked isocyanate-terminated prepolymer and an adhesion promoter which is non-reactive therewith. Moreover, the present invention relates to such a urethane sealant composition or coating
35 admixture which is essentially or desirably free of any organosilane compounds which are reactive with the blocked isocyanate-terminated prepolymer. The blends of the present invention when a one-part system desirably contain a polyimine curing agent and when a two-part system generally contain a polyamine curing agent. The blends can also contain various conventional additives and the like and upon cure yield a sealant or coating having improved physical properties and especially improved adhesion properties.

40 Considering the urethane prepolymers, the urethane prepolymers of the present invention are generally made from a polyisocyanate and any conventional intermediate utilized in the preparation of urethane sealants or coatings. Thus, the intermediate can be a polyether polyol, a polyester polyol, and the like wherein the polyol is a diol or a triol. Such urethane intermediates are well known to the art and to the literature. Specific examples include polyethylene ether diols or triols, polypropylene ether diols or triols,
45 polybutylene ether diols or triols, polytetramethylene ether diols or triols, and block copolymers of such diols and triols, and/or blends thereof. Specific examples of hydroxyl-terminated polyesters include any hydroxy-terminated polyester prepared from poly-basic acids or anhydrides as for example adipic acid and phthalic anhydride, and polyols in which the hydroxyl functionality of the polyester prepolymer is greater than 2, and preferably greater than 2.3. The intermediates generally have a molecular weight of from about
50 1,000 to about 25,000.

The prepolymers of the present invention are made by reacting the above-noted polyol intermediates with a polyisocyanate generally having the formula $R(NCO)_n$ wherein n is 2, 3 or 4 and R is an aliphatic, an aromatic, or an aliphatic substituted aromatic having from 4 to 20 carbon atoms and preferably from 6 to 15 carbon atoms. Desirably the aliphatic groups are alkyl groups. Examples of specific di- or triisocyanates
55 which can be utilized include p,p'-triisocyanato triphenyl methane, p,p'-diisocyanato diphenyl methane (MDI), hexamethylene diisocyanate, naphthalene-1,5-diisocyanate, and various isomers of toluene diisocyanates (TDI) such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, and mixtures thereof. MDI and TDI are preferred. Inasmuch as an adhesive type composition is desired, the equivalent weight ratio of

5

10

2

2



like.

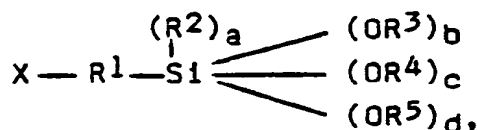
When a one part system is utilized, that is a composition in which all of the components of the polyurethane sealant or coating are contained together, a polyimine curing agent is generally utilized. The polyimines will not react with the blocked isocyanate-terminated prepolymer unless exposed to moisture as upon application of the sealant. Various polyimines can be prepared by reacting any of the above polyamine compounds with either a ketone or an aldehyde as well known to those skilled in the art and to the literature. The end result is the production of various ketimine compounds or aldimine compounds. Examples of specific ketimine type compounds which can be utilized are set forth in U.S. Patent No. 4,507,443 which is hereby fully incorporated by reference.

Regardless of whether a one part or two part system is utilized, the amount of the polyamine or polyimine curing agent is from about 0.6 to about 1.5 weight equivalents and preferably 0.8 to 1.2 weight equivalents per equivalent of a blocked isocyanate.

When a two component system is utilized, as noted above, one of the components contains the prepolymer and the second component contains the curing agent. The curing agent component generally contains the amine curing agent, and various additives in conventional amounts, if desired, such as various plasticizers, pigments, thickeners, drying agents, and the like. The prepolymer or base component contains various conventional additives or compounding ingredients such as fillers, thixotropic agents, extenders, pigments, plasticizers, UV absorbers, solvents, and the like. Typically, the prepolymer component contains large amounts of a filler such as talc, various types of silicates, various types of clays, calcium carbonate, and the like, in an amount of from about 60 to about 200 parts by weight per 100 parts by weight of the prepolymer; a thickening agent such as a thixotropic compound in an amount of from 0 to about 30 parts by weight per 100 parts by weight of the prepolymer; UV absorbers in an amount of usually less than 1 or 2 parts by weight per 100 parts by weight of the prepolymer; and plasticizers in an amount of from about 0 to about 50 parts by weight per 100 parts by weight of the prepolymer. Solvents, which are generally utilized to adjust the viscosity of the prepolymer or base component to a desired range, constitute generally less than 10 percent volatility of the total prepolymer component for sealant compositions. In coating compositions, the amount of solvent is generally higher.

The present invention is the utilization of certain types of adhesion promoters which are non-reactive with the blocked isocyanate-terminated prepolymers. That is unlike U.S. Patent No. 4,507,443, the adhesion promoters of the present invention are specific functional organic silane or functional organic siloxane compounds which do not react with the blocked isocyanate prepolymers. Accordingly, the sealant compositions and coating admixtures of the present invention are essentially free from, exclude, or do not contain organosilane compounds which react with the blocked isocyanate-terminated prepolymers. Such isocyanate reactive organosilane compounds are not within the ambit of the present invention inasmuch as their reaction has found to degrade mechanical properties such as movement capability. It has been found, however, that the use of an epoxysilane or an epoxysilane, an isocyanatosilane, or an isocyanatosiloxane, or a ketiminosilane or a ketiminosiloxane improves various physical mechanical properties such as elongation, modulus, movement capability, as well as adhesion.

The various functional silane compounds of the present invention which are nonreactive with blocked isocyanates can generally be represented by the formula



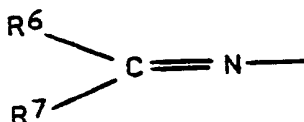
or a siloxane derivative thereof, which X is a functional group such as an epoxy group, an isocyanate, or a ketimine. R¹ is an intermediate or linking hydrocarbon group such as an aliphatic, desirably an alkyl, having from 1 to 16 carbon atoms with from 2 to 6 carbon atoms being preferred. A preferred R¹ group is propyl. R¹ can also be a cycloaliphatic such as a cyclo alkyl having from 4 to 8 carbon atoms. A less desired R¹ group is an aromatic or an alkyl substituted aromatic having from 6 to 15 carbon atoms. The R² group is an aliphatic, such as an alkyl, having from 1 to 25 carbon atoms or less desirably an aromatic or an alkyl substituted aromatic having from 6 to 15 carbon atoms. The number of such "a" groups is 0, 1, or 2. Each alkoxy group, independently, is 0 or 1, that is "b", "c", and "d" is 0 or 1, with the proviso that "a" + "b" + "c" + "d" = 3. R³, R⁴, and R⁵, independently is an alkyl having from 1 to 10 carbon atoms, with 1 to 4 carbon atoms being preferred, or an aromatic or an alkyl substituted aromatic having from 6 to 12 carbon atoms. Preferably all three alkoxy groups exist with said groups being methoxy. Thus, trimethoxysilyl is a

highly preferred silane group.

The various X groups, as noted, can be an epoxy group, an isocyanato group, or a ketimino group. Numerous epoxy groups can exist. For example, the epoxy group can be an epoxy group per se (i.e., ethylene oxide), glycidoxy - a preferred group, 2-alkylglycidoxy wherein the alkyl group has from 1 to 4 carbon atoms with methyl being desired, an epoxycycloalkylene group wherein the alkylene group has from 4 to 10 carbon atoms with epoxycyclohexyl being desired. Inasmuch as the specific epoxy group of glycidoxy is preferred, a preferred epoxysilane of the above formula is gamma-glycidoxypropyltrimethoxysilane.

With regard to X being an isocyanate group, it is precisely that, that is an NCO group. A preferred isocyanatosilane is isocyanatopropyltrimethoxysilane.

Considering the ketiminosilanes, the X portion has the formula



where R^6 and R^7 , independently, is an aliphatic and desirably an alkyl having from 1 to 10 carbon atoms and preferably from 1 to 4 carbon atoms, less desirably an aromatic or an alkyl substituted aromatic having from 6 to 15 carbon atoms, or is hydrogen. A preferred ketiminosilane is the methylisobutylketone based ketimine of gamma-aminopropyltrimethoxysilane.

The epoxysilanes, the isocyanatesiloxanes, and the ketiminosiloxanes, are merely siloxane oligomers of the above-noted epoxysilanes, isocyanatosilanes or ketiminosilanes. The oligomers can be a dimer, trimer, etc. and can be defined as having 2 to about 50 repeating units of the silicon atom.

Utilizing the specific functional silane or siloxane compounds of the present invention which are nonreactive with blocked isocyanates, it has been found that better physical properties are obtained as set forth hereinafter. In contrast, the different organosilanes previously utilized which reacted with free isocyanate groups as well as with blocked isocyanate groups did not yield the improved properties of the present invention.

Urethane sealants of the present invention can be utilized as caulking compounds for windows, panels, concrete, masonry, stone, and the like. When utilized as a protective coating composition, a solvent material such as toluene, benzene, xylene, hexane, heptane, and the like, is generally added to provide a coating composition having a consistency suitable for application as by spraying, bushing, roll coating, and the like.

The invention will be better understood by reference to the following examples.

EXAMPLE 1

40

(Control)

A blocked isocyanate-terminated polymer was formed according to the following procedure.

About 2000 parts by weight of a polyol consisting of a copolymer of propyleneoxide with ethyleneoxide having an hydroxyl number of 26 was admixed with 556 parts by weight of toluene and azeotroped to remove 356 parts by weight of toluene. After cooling under nitrogen atmosphere, 166 parts by weight of an 80/20 weight percent mixture of 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate were added at room temperature. The resulting mixture was heated to 90°C and held at that temperature for three hours to form the isocyanate terminated prepolymer. About 209 parts by weight of nonylphenol then were added to the reaction mixture and the mixture was maintained at 90° for one hour. About 0.2 parts by weight of stannous octoate (a catalyst for promoting blocking of the isocyanate terminated polymer) was added to the mixture and the mixture was maintained at 90°C for an additional two hours. The resulting blocked isocyanate terminated prepolymer was formulated according to the following recipe.

55

Blocked isocyanate terminated polymer described above	100 parts
Thixcin R, a Thixotrope, made by NL Industries	15 parts
Benzoflex, 9-88, a plasticizer made by Monsanto	26 parts
Calcium carbonate	60 parts
Paraffin wax	2.2 parts
Process oil	4.4 parts
A ketimine prepared from Jeffamine D-400, and methylisobutylketone	10.7 parts

10 Samples prepared from above formulation were cured for one week at room temperature, one week at 120°F, and one week at 158°F. Physical properties of the cured sample are given in Table I and are used as the control for Examples 2, 3 and 4.

15 EXAMPLE 2

A prepolymer described in Example 1 was formulated according to the following recipe.

Blocked isocyanate-based polymer	100 parts
Thixcin-R	15 parts
Benzoflex 9-88	26 parts
Calcium Carbonate	60 parts
Paraffin wax	2.2 parts
Process Oil	4.4 parts
Ketimine from Jeffamine D-400 and Methyl isobutyl ketone	10.9 parts
Gamma-glycidoxypyriltrimethoxysilane	0.2 parts

30 Samples prepared according to the above formulation were cured for one week at room temperature, one week at 120°F, and for one week at 158°F. Physical properties and the adhesion data of the cured samples is given in Table I. Data in Table I clearly shows that addition of epoxysilanes such as gamma-glycidoxypyril trimethoxysilane in small concentration significantly improves the adhesion without effecting the physical properties.

35 EXAMPLE 3

40 100 parts of methylisobutylketone were azeotroped and 52 parts by weight of methylisobutylketone were removed to dry the methylisobutylketone. To the remaining methylisobutylketone, 45 parts by weight of gamma-aminopropyltrimethoxysilane is added at room temperature. The above reaction was stirred at room temperature for 30 minutes and then heated to 60°C and held at that temperature for 4.5 hours. Excess methylisobutylketone and methanol was then removed by distillation. A ketiminosiloxane, so
45 prepared is used in the following formulation.

Blocked isocyanate-based polymer	100 parts
Thixcin R	15 parts
Benzoflex	26 parts
Calcium carbonate	60 parts
Paraffin wax	2.2 parts
Process Oil	4.4 parts
Ketimine from Jeffamine D-400 and Methylisobutyl ketone	10.5 parts
Ketiminosiloxane prepared as set forth above	0.2 parts

50 Samples prepared according to the above formulation were cured according to the procedure given in Example 1. Physical properties and the adhesion data for the cured samples are given in Table I. Data in

Table I clearly shows that addition of a small amount of ketiminosiloxane improved the adhesion without significantly effecting physical properties.

EXAMPLE 4

A prepolymer described in Example 1 was formulated according to the following recipe.

Blocked isocyanate-based prepolymer	100 parts
Thixcin R	15 parts
Benzoflex	26 parts
Calcium carbonate	60 parts
Paraffin wax	2.2 parts
Process Oil	4.4 parts
Ketimine from Jeffamine D-400 and Methylisobutyl ketone	10.5 parts
Isocyanatopropyltrimethoxysilane	0.3 parts

Samples prepared from the above formulation were cured according to the procedure given in Example 1. Physical properties and the adhesion data for the cured samples is given in Table I. Data in Table I clearly shows that addition of a small amount of isocyanatosilanes improves both adhesion as well as physical properties of the cured sample.

TABLE I

	Example 1 (Control)	Example 2 (Epoxyasilane)	Example 3 (Ketiminosilane)	Example 4 (Isocyanatosilane)
Elongation %	983	975	887	1350
100% Modulus, psi	68	67	87	66
Tensile strength, psi	196	160	258	268
Dry Adhesion Glass	100% AD	100% COH	100% COH	100% COH
	10.1 pli	57.4 pli	50.0 pli	49.2 pli
Anodized Aluminum	100% ADH	100% COH	100% ADH	100% ADH
	5.6 pli	49.7 pli	40.2 pli	45.0 pli
Milled Aluminum	100% ADH	100% ADH	100% ADH	100% ADH
	2.3 pli	9.6 pli	8.2 pli	7.6 pli
Notes:	COH represents cohesive nature of sealant failure ADH represents adhesive nature of sealant failure pli represents pounds per linear inch psi represents pounds per square inch			

EXAMPLE 5

A blocked isocyanate-based prepolymer was prepared using 3000 grams of polyol consisting of a copolymer of propyleneoxide with ethyleneoxide, 150 grams toluene, 259.8 grams of an 80/20 weight percent mixture of 2,4-tolylenediisocyanate and 2,6-tolydiisocyanate, and 344 grams of nonlyphenol according to a procedure similar to the one described in Example 1.

A prepolymer so prepared was formulated according to formulation given in Table II.

TABLE II

	Control	5A	5B	5C	5D
Prepolymer (g)	100	100	100	100	100
Thixcin R (g)	15	15	15	15	15
Benzoflex (g)	26	26	26	26	26
Calcium carbonate	60	60	60	60	60
Paraffin wax (g)	2.2	2.2	2.2	2.2	2.2
Process oil (g)	4.4	4.4	4.4	4.4	4.4
MIMS (g)	0	1.2	1.2	1.2	1.2
Ketamine					
(see Note 1) (g)	10.7	10.87	10.87	10.87	10.87
Gamma-glycidioxypropyl-trimethoxypropylsilane	0	0.4	0.5	0.6	0.7
Elongation, %	983	944	835	949	901
100% Modulus, psi	68	72	73	71	64
Tensile Strength, psi	196	156	158	164	165
Dry Adhesion	100% ADH	100% COH	100% COH	100% COH	100% COH
Glass	10.1 pli	64.5 pli	62.0 pli	61.5 pli	49.3 pli
Anodized Aluminum	100% ADH	100% COH	100% COH	100% COH	100% COH
	5.6 pli	58.3 pli	48.5 pli	41.0 pli	50.7 pli
Milled Aluminum	100 ADH	100% COH	100% COH	100% COH	100% COH
	2.3 pli	64.5 pli	53.1 pli	50.8 pli	55.1 pli
Concrete	--	100% ADH	100% ADH	100% ADH	100% ADH
	--	45.0 pli	43.5 pli	41.7 pli	39.6 pli

TABLE II (continued)

	CONTROL	5A	5B	5C	5D
Adhesion after Water Immersion (see Note 2)					
Glass	-	100% COH 37.6 pli	100% COH 54.7 pli	100% COH 29.4 pli	100% COH 46.7 pli
Anodized Aluminum	-	100% COH 61.0 pli	100% COH 36.7 pli	100% COH 45.8 pli	100% COH 35.3 pli
Milled Aluminum	-	100% COH 35.0 pli	100% COH 60.5 pli	100% COH 41.9 pli	100% COH 43.6 pli
Concrete	-	100% ADH 30.5 pli	100% ADH 24.7 pli	100% ADH 31.3 pli	100% ADH 25.0 pli

1. The ketimine was prepared by reacting Jeffamine D-400 with methyl isobutyl ketone.
The procedure for preparing this ketimine is disclosed in U.S. Patent No. 4,507,443.

2. Since the adhesion before immersion was adhesive in nature, it was not tested after water immersion.

Data in Examples 2 through 5 clearly shows that the mechanical properties are not effected significantly when the epoxysilane level was varied from 0.2 parts to 0.7 parts per 100 grams of the polymer. This data further shows that adequate adhesion is obtained with 0.4 or more parts of the epoxysilane per 100 grams of prepolymer.

EXAMPLE 6

A blocked isocyanate terminated polymer was formed according to the following procedure.

About 181.9 pounds of a polyol consisting of a copolymer of propyleneoxide with ethyleneoxide with an hydroxyl number of 26.7 was admixed with 18.75 pounds of toluene. To this mixture, 15.82 pounds of an 80/20 weight percent mixture of 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate were added at room temperature. The resulting mixture was heated to 85°C and held at that temperature for two hours. Nonylphenol in an amount of 20.9 pounds was then added to the mixture and the mixture was maintained for one hour at 85°C. About 6.2 grams of stannous octoate were added to the mixture and the mixture was maintained for two hours and fifteen minutes. The resulting reaction product was a blocked isocyanate terminated prepolymer. This prepolymer was used in Examples 6, 7, and 8. Recipe and the sealant evaluation is given in Table III.

TABLE III

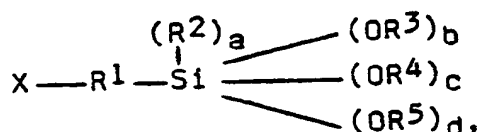
	EXAMPLE 6	EXAMPLE 7	EXAMPLE 8
Polymer	200	200	200
Thixcin R	30	30	30
Benzoflex 9-88	52	52	52
Calcium Carbonate	120	120	120
Paraffin Wax	4.5	4.5	4.5
Process Oil	8.9	8.9	8.9
Ketimine prepared from Jeffamine D-400 and Methylisobutyl ketone	17.2	17.2	17.2
Gamma-Aminopropyltrimethoxysilane	0.6	0.0	0.0
Ketiminosiloxane (see Example 3)	0.0	0.6	0.0
Gamma-Glycidoxypopyltrimethoxysilane	0.0	0.0	0.6
Elongation, %	700	900	1100
100% Modulus, psi	94	82	75
Tensile strength, psi	153	144	121
Adhesion (See Note 1)			
Concrete, pli	53.1	51.2	23.8
Glass, pli	42.3	51.5	36.1
Anodized Aluminum, pli	47.7	59.5	46.6
Milled Aluminum, pli	42.3	41.5	44.6
Note 1.			
Nature of adhesion was cohesive in all these samples.			

The data in Examples 6, 7 and 8 show the use of three different types of nonreactive silanes produce good adhesion results.

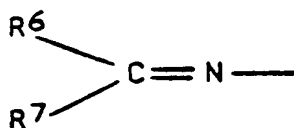
While in accordance with the Patent Statutes, the best mode and preferred embodiment has been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

Claims

1. A sealant composition or coating admixture, comprising:
 a blend of a blocked isocyanate prepolymer, a functional silane or siloxane adhesion promoter non-reactive
 with said blocked isocyanate-terminated prepolymer, and an effective amount of a polyamine or a
 polyamine curing agent capable of curing the sealant composition or the coating admixture, said blend
 being substantially free of organosilanes which are reactive with said blocked isocyanate prepolymer, the
 amount of said functional silane or siloxane adhesion promoter being from about 0.1 to about 10 parts by
 weight based upon 100 parts by weight of said prepolymer.
2. A sealing composition or coating admixture according to Claim 1, wherein said functional silane
 adhesion promoter non-reactive with said blocked isocyanate-terminated prepolymer has the formula



- or a siloxane derivative thereof,
 wherein R¹ is an aliphatic having from 1 to 16 carbon atoms, a cycloaliphatic having from 4 to 8 carbon
 atoms, or an aromatic or an alkyl substituted aromatic having from 6 to 15 carbon atoms, wherein R² is an
 aliphatic having from 1 to 25 carbon atoms, or an aromatic or an alkyl substituted aromatic having from 6 to
 15 carbon atoms, wherein R³, R⁴, and R⁵, independently, is an alkyl having from 1 to 10 carbon atoms, an
 aromatic or an alkyl substituted aromatic having from 6 to 12 carbon atoms, wherein "a" is 0, 1, or 2,
 wherein "b", "c", and "d", independently, is 0 or 1, wherein "a" + "b" + "c" + "d" = 3, and wherein X is
 an epoxy group, an isocyanato group, or a ketimine group.
3. A sealing composition or coating admixture according to Claim 2, wherein X is an epoxy group,
 wherein said epoxy group is epoxy, glycidoxy, 2-alkylglycidoxy wherein said alkyl group has from 1 to 4
 carbon atoms, or an epoxycycloalkylene wherein said alkylene has from 4 to 10 carbon atoms.
4. A sealing composition or coating admixture according to Claim 3, wherein R¹ is an alkyl having from
 2 to 6 carbon atoms, or a cycloalkyl having from 4 to 8 carbon atoms, wherein R² is an alkyl having from 1
 to 25 carbon atoms, and wherein R³, R⁴, and R⁵, independently, is an alkyl having from 1 to 4 carbon
 atoms.
5. A sealing composition or coating admixture according to Claim 4, wherein said epoxysilane adhesion
 promoter is glycidoxypropyltrimethoxysilane.
6. A sealing composition or coating admixture according to Claim 3, wherein said adhesion promoter is
 a siloxane derivative of the compositions of Claim 3 and has from 2 to 50 repeating groups therein.
7. A sealing composition or coating admixture according to Claim 5, wherein said adhesion promoter is
 a siloxane oligomer of glycidoxypropyltrimethoxysilane having from 2 to 50 siloxane repeating units.
8. A sealing composition or coating admixture according to Claim 2, wherein X is an isocyanato group,
 wherein R¹ is an alkyl having from 2 to 6 carbon atoms, or a cycloalkyl having from 4 to 8 carbon atoms,
 wherein R² is an alkyl having from 1 to 25 carbon atoms, wherein R³, R⁴, and R⁵, independently, is an alkyl
 having from 1 to 4 carbon atoms.
9. A sealing composition or coating admixture according to Claim 8, wherein said adhesion promoter is
 isocyanatopropyltrimethoxysilane.
10. A sealing composition or coating admixture according to Claim 8, wherein said adhesion promoter is
 a siloxane derivative of said isocyanato compound and has from 2 to 50 siloxane repeating units therein.
11. A sealing composition or coating admixture according to Claim 9, wherein said adhesion promoter is
 a siloxane derivative of said isocyanatopropyltrimethoxysilane and has from 2 to 50 siloxane repeating units
 therein.
12. A sealing composition or coating admixture according to Claim 2, wherein X is a ketimine group,
 wherein said ketimine group has the formula



5

wherein R⁵ and R⁷, independently, is an aliphatic having from 1 to 10 carbon atoms, an aromatic or an alkyl substituted aromatic having from 6 to 15 carbon atoms, or hydrogen.

10 13. A sealing composition or coating admixture according to Claim 12, wherein R¹ is an alkyl having from 2 to 6 carbon atoms, or a cycloalkyl having from 4 to 8 carbon atoms, wherein R² is an alkyl having from 1 to 25 carbon atoms, wherein R³, R⁴, and R⁵, independently, is an alkyl having from 1 to 4 carbon atoms.

14. A sealing composition or coating admixture according to Claim 13, wherein said adhesion promoter is the methylisobutylketone ketimine of gamma-aminopropyltrimethoxysilane.

15 15. A sealing composition or coating admixture according to Claim 13, wherein said adhesion promoter is a siloxane derivative of said ketimine and has from 2 to about 50 siloxane repeating units therein.

16. A sealing composition or coating admixture according to Claim 14, wherein said adhesion promoter is a siloxane of said ketimine and has from 2 to 50 siloxane repeating units therein.

17. A sealing composition or coating admixture according to Claim 2, wherein said sealing composition or coating admixture is cured.

18. A sealing composition or coating admixture according to Claim 4, wherein said sealing composition or coating admixture is cured.

19. A sealing composition or coating admixture according to Claim 8, wherein said sealing composition or coating admixture is cured.

20. A sealing composition or coating admixture according to Claim 13, wherein said sealing composition or coating admixture is cured.

30

35

40

45

50

55

THIS PAGE BLANK (USPTO)

12

EUROPEAN PATENT APPLICATION

21 Application number: **89109014.4**

51 Int. Cl.⁴: **C 09 K 3/10**
C 08 G 18/10

22 Date of filing: **19.05.89**

30 Priority: **23.05.88 US 197493**

43 Date of publication of application:
29.11.89 Bulletin 89/48

84 Designated Contracting States: **DE FR GB**

88 Date of deferred publication of search report:
31.01.90 Bulletin 90/05

71 Applicant: **TREMCO INCORPORATED**
10 701, Shaker Boulevard
Cleveland, Ohio 44104 (US)

72 Inventor: **Bandlish, Baldev K.**
4633 Bradford
S. Euclid Ohio 44121 (US)

74 Representative: **von Kreisler, Alek, Dipl.-Chem. et al**
Patentanwälte Von Kreisler-Settling-Werner
Deichmannhaus am Hauptbahnhof
D-5000 Köln 1 (DE)

54 Sealant compositions or coating mixtures containing functional silane or siloxane adhesion promoters nonreactive with blocked isocyanates.

57 A sealant or coating composition admixture contains a blocked isocyanate-terminated prepolymer in which generally all of the NCO groups are blocked, a curing agent such as a polyamine or a polyimine, and a functional silane or siloxane nonreactive with blocked isocyanates. The sealants or coating compositions when cured have improved properties such as adhesion.



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 89109014.4
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP - A2 - 0 230 666 (ESSEX SPECIALTA PRODUCTS) * Page 2, lines 26-42 *	1-3	C 09 K 3/10 C 08 G 18/10
A	US - A - 4 382 991 (POLLMANN) * Claim 1 *	1,2	
A	DERWENT ACCESSION NO. 78-35485A (20) Questel Telesystems (WPI) DERWENT PUBLICATIONS LTD., London * Abstract * & JP-A-53-035 798 (MITSUI NISSO) -----	1,2	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 09 K C 08 G
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 16-11-1989	Examiner WILFLINGER
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO Form 1503, 03.82